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Eco-efficient recovery of non-volatile products from fermentation broth: aliphatic diols

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Abstract

Fermentation can be used to obtain a wide variety of valuable high-boiling components. Among these components, microorganisms can produce aliphatic diols (e.g. propanediols, butanediols, etc.) in significant concentrations (e.g. 5–15 wt.%). Nonetheless, the high boiling points of these components, presence of microorganisms, and formation of by-products complicate recovery after fermentation. Hence, this perspective offers valuable insights into downstream processing options. A novel methodology was developed for recovering high-boiling components from dilute aqueous solutions, whereby both light and heavy impurities are present. The main steps in the proposed methodology are heat pump-assisted preconcentration and final purification in a dividing-wall column. These steps allow effective separation of high-purity product from water, light and heavy impurities. Furthermore, processes for recovery of 1,3-propanediol, 2,3-, 1,4- and 1,3-butanediol, designed according to the proposed methodology, were compared. Downstream processing performance is mainly determined by the product concentration in the fermentation broth, but is also influenced by the amount of impurities in the broth.

Keywords: Distillation; Downstream Processing; Industrial biotechnology; Process Intensification; Process Technology; Sustainable Processing

INTRODUCTION

Aliphatic diols are typical examples of valuable chemicals that can be produced in significant amounts by fermentation. Fermentative production of these chemicals has several drawbacks that complicate downstream processing. The first challenge for the downstream processing is product concentration in the fermentation broth. Even though these diols are less hydrophobic than mono-alcohols, hence less inhibiting, concentrations achieved in the fermentation broths are modest (< 15 wt.%). Therefore, the feed stream to the recovery process is highly diluted. Consequently, large equipment units are required to achieve sufficient production capacity for an industrially relevant scale.

Secondly, these diols are high-boiling components (see Table 1), with a boiling point of way over 100 °C (the boiling point of water at atmospheric pressure).[1] Thus, they cannot be simply removed from the broth by evaporation. On the contrary, evaporating large amounts of water can be very energy-intensive, if poorly designed, possibly resulting in high operating costs.

An additional challenge for the recovery process is the common presence of by-products (e.g. different carboxylic acids, ethanol, etc.).[2-6] Depending on concentrations of these by-products, it may be worth valorizing them. Valorizing by-products could improve downstream processing performance by reducing specific costs and energy requirements. However, recovering by-products that are present in very small amounts may significantly increase capital costs due to new equipment units, without bringing major benefits.

Lastly, microorganisms, residual substrate, biopolymers, and inorganics are present in the fermentation broth that is sent to product recovery. To allow biomass recycling, these microorganisms should preferably be separated from the broth without harming their viability.

Considering the above-mentioned challenges, several steps are required to obtain a high-purity final product, separate microorganisms, and possibly recover some of the by-products. Consequently, the costs of downstream processing may be a significant contributor to the total production costs. Improving downstream operations is expected to enhance overall process performance by reducing these costs, while application of process intensification principles presents opportunities to improve energy efficiency. In this context, we propose a methodology for recovering high-boiling products from dilute aqueous

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Table 1. Boiling points (at 1 bar) of the diols commonly produced by the fermentation

Component	Boiling point (°C)
2,3-butanediol (2,3-BDO)	180.7
1,3-butanediol (1,3-BDO)	207.5
1,3-propanediol (1,3-PDO)	214.2
1,4-butanediol (1,4-BDO)	228.0

solutions containing both light and heavy impurities. This perspective offers valuable insights into the recovery of aliphatic diols from the fermentation broth, with an emphasis on the purification of desalted and clarified aqueous solution.

DOWNSTREAM PROCESSING OF DIOLS AFTER FERMENTATION

Performance of the downstream processing in the fermentative production of diols has been analyzed using 1,3-propanediol (PDO), 2,3-, 1,4- and 1,3-butanediols (BDOs) as representative examples. These chemicals were chosen as their production by fermentation has recently attracted much attention. Among others, companies such as DuPont[5,7] LanzaTech, BioPrincipia,[8-10] Genomatica and Novamont[11-13] are actively developing fermentative production of these valuable chemicals. To the best of our knowledge, fermentative production of various other diols (e.g., ethylene glycol, 1,2-propanediol, pentanediols)[14] has been a topic of research but remains in early stages of development. Consequently, these were not included in the present study.

Due to the complexity of the fermentation broth, several steps are often needed in the recovery process.[15] Since both light and heavy impurities are present, PDO/BDO is the middle-boiling product in the fermentation broth. Hence, it would be very energy-intensive to use simple distillation as an *in-situ* product recovery technique. Furthermore, the high boiling point of PDO/BDO would require usage of extreme vacuum conditions to ensure that temperatures would not harm microbial viability. For these reasons, initial separation steps, such as filtration and ion exchange, are typically employed to remove biomass and majority of large organic and inorganic molecules. These operations are well-established in industrial fermentation processes and are therefore not the focus of this work. Instead, the emphasis is placed on advancing the subsequent stages of the recovery process, which are often the most energy-intensive.

A result of these initial separation steps is a desalted and clarified aqueous stream containing PDO/BDO product and some by-products. Thus, additional preconcentration and final purification steps are required to separate water, light and heavy impurities and recover a high-purity final product. Distillation plays a major role as the main recovery technique in these steps. It is a mature separation technique, commonly used on an industrial scale. It does not require the usage of any additional chemicals that would complicate the downstream processing and influence the environmental impact of the process. Moreover, since none of the considered diols forms an azeotrope with water, there is no need for more complex techniques such as extractive or azeotropic distillation. Nonetheless, the preconcentration step may be very energy-intensive due to large amounts of water that need to be removed. The final purification step is complex due to common presence of both lowerand higher-boiling impurities. Hence, advanced distillation techniques are needed to ensure the energy efficiency of the overall bioprocess. In that respect, we propose a methodology for recovering high-boiling products from dilute aqueous solutions containing both light and heavy impurities. This methodology is further applied to the preconcentration and final purification steps in the PDO/BDO recovery after fermentation. Furthermore, it may facilitate the development of industrial-scale fermentative processes by indicating the costs of the recovery process. These data should be coupled with relevant data from the upstream process to obtain a full picture of the bioprocess performance.

However, it should be noted that in case a high-boiling product is present in very small concentrations in the fermentation broth (e.g. achievable concentration of 2-phenylethanol in the fermentation broth is <0.3 wt.%), distillation would have to be coupled with some other technique for *in-situ* product recovery (e.g. liquid–liquid extraction, product adsorption, etc.). In this case, distillation would be used in the final purification to separate the valuable product from the used solvent. Thus, a slightly different approach would be needed. This is not covered by the presented methodology, which focuses on the recovery of high-boiling products from a dilute aqueous solution.

METHODOLOGY FOR THE RECOVERY OF NON-VOLATILE PRODUCTS FROM AQUEOUS SOLUTION

The proposed methodology for the recovery of high-boiling products from a dilute aqueous solution is pictured in Fig. 1.

Initially, most of the water, with some light impurities (e.g. ethanol if present), should be removed from the rest of the mixture containing valuable high-boiling products. Separating water at this stage would significantly reduce equipment size and energy requirements in the final purification part of the process. We propose a multi-stage preconcentration step in adistillation column in which most light components are removed without losing the main product.[16,17] Even though possible, not all water and light impurities should be separated in this step. This would limit implementation of heat pump systems, as it would result in a large temperature difference between top and the bottom of the preconcentration column. Alternatively, with the proper choice of operating parameters, it is possible to separate most of the water, with some light impurities, while keeping the top and bottom column temperature sufficiently close for implementing heat pumps. Mechanical vapor recompression (MVR) is a state-of-the-art industrial heat pump system that can be applied when separating close-boiling components. It implies compressing vapor from top of the column and using it instead of an external heating utility to evaporate the bottom liquid in a reboiler.[18] Hence, electrical energy required to power the compressor can replace much higher thermal energy that would be needed to heat the reboiler. Furthermore, implementation of the MVR system allows complete (green) electrification of the preconcentration step. If needed, reduced pressure can be applied to this column to avoid the formation of high temperatures. An aqueous stream separated as the top product from the preconcentration column can be reused in the fermentation (if high purity) or sent to the wastewater treatment (if impurities are present). The bottom stream from this column contains PDO/BDO products with some water and remaining light and heavy impurities. This stream needs to be sent to the final purification to obtain a high-purity product.

The final purification part of the recovery process consists of two steps. Initially, the remaining water and light impurities should be separated as a top product from the distillation column. Secondly, the main product must be separated (as a top product) from the remaining heavy impurities (that are obtained as a bottom product). Thus, a sequence of two distillation columns is required for this separation. Alternatively, these two columns can be merged into one dividing-wall column (DWC). This equipment unit may reduce operating costs by improving the energy efficiency of the separation. Additionally, it also reduces capital costs by merging two column shells into one, decreasing the number of needed heat exchangers and reducing the required area.[19] Nonetheless, DWC may not always be the best option, and it should be compared to the sequence of distillation columns for a specific composition of the fermentation broth.[20] A reduced pressure operation is likely to be needed for the final purification part of the process due to the high boiling temperatures of these diols (see Table 1). Depending on the amounts of light or heavy impurities, it may be worth valorising some of them. Otherwise, these streams should be sent to the waste treatment or burned for energy, and appropriate costs must be accounted for.

After designing the preconcentration step, enhanced by the MVR system, and the final purification step, additional heat integration opportunities should be considered to further minimize energy requirements. Finally, once the final process flowsheet is developed, economic and sustainability analysis should be performed to evaluate the impact of the developed process.

To the best of our knowledge, the proposed methodology differs significantly from the published studies on the purification of diols after fermentation. So far, a simple sequence of distillation columns has been proposed to remove present water and purify PDO from light and heavy impurities.[21-25] On the contrary, more research has been done on the recovery of BDOs (mainly 2,3-BDO). However, a multistage preconcentration step in which

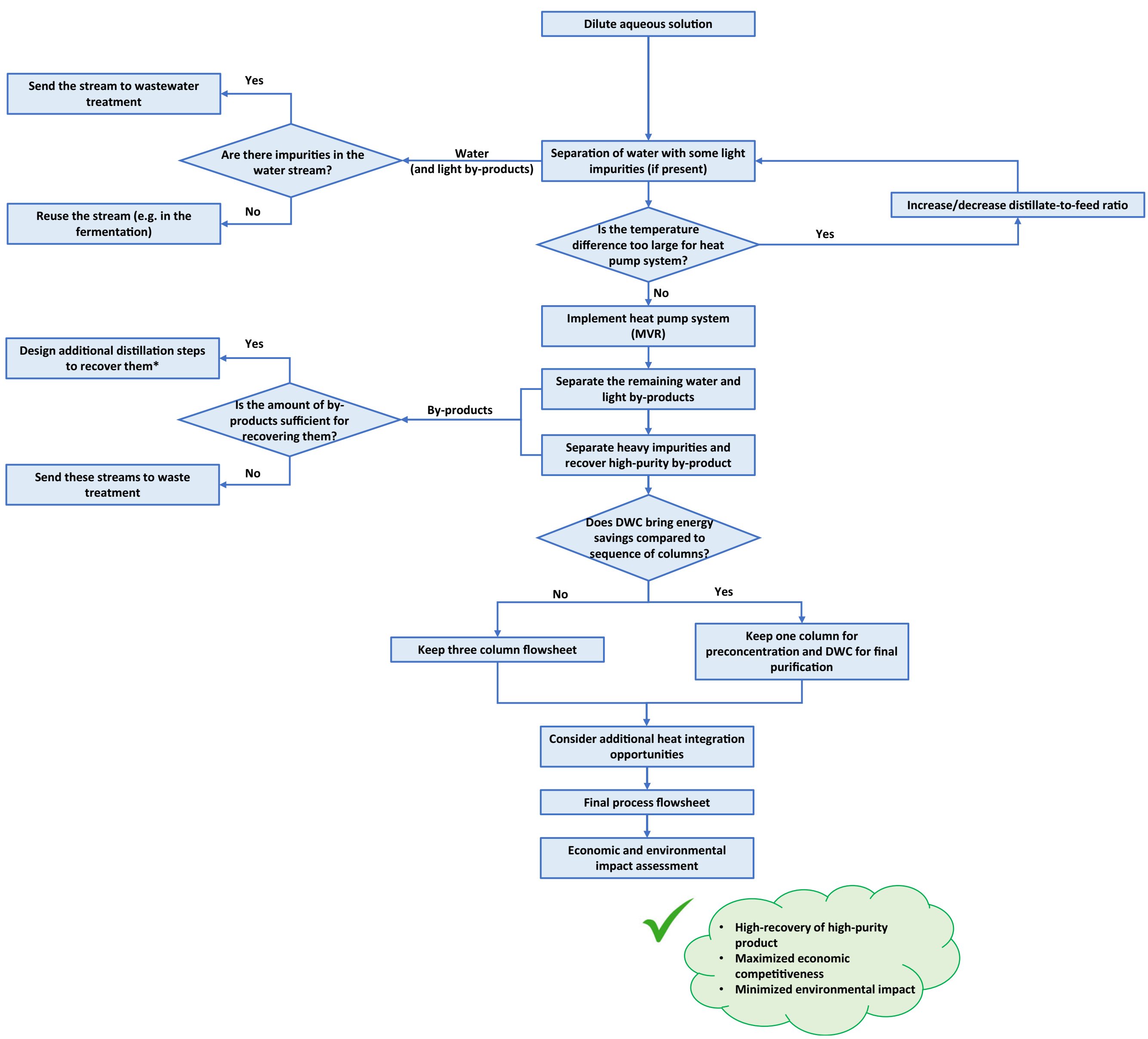

Figure 1. Proposed methodology for purification of high-boiling products from aqueous. *As previously shown for the valorization of by-products in 1,3-PDO fermentation.

most of the water and light components are removed without losing valuable product has not been proposed. Some studies considered an evaporation step in a flash unit before the final purification.[2,26] In this step, smaller amounts of impurities were removed while most of the light components were sent to the final purification. As a result, the final step required larger equipment units with higher thermal energy demands. Moreover, in the final purification step, BDO was recovered as a side stream, while water with light by-products was removed as the top product, and heavy by-products were obtained at the bottom of the column. Consequently, the temperature difference between the top and the bottom of the column was too large, and the heat pump system could only be used to preheat the feed stream, but not to evaporate the bottom liquid. An alternative suggested removing all light components in a flash evaporator unit before the final distillation. The top vapor from the distillation column could be compressed and used to partially heat the evaporator unit.[27] However, one-stage separation caused BDO loss. Furthermore, the installed heat pump system could not supply sufficient heat in the flash unit. On the contrary, we propose a multi-stage preconcentration step in the heat pump-assisted distillation column C1 in which most light components are removed without losing BDO product. Thus, the reboiler duty and equipment size in the final purification step will be smaller due to significantly reduced flowrate of the feed stream to this step. Additionally, the MVR system in column C1 can completely cover the thermal energy requirements of the preconcentration step. As this operation is very energy intensive, the implemented heat pump system drastically reduces the energy requirements of the total downstream process.[16,17]

EFFECTS OF DIOL PRODUCT ON DOWNSTREAM PROCESSING PERFORMANCE

A generic block flow diagram for the purification of high-boiling products from the dilute fermentation broth was derived (see Fig. 2) following the previously explained methodology. A comparison between the downstream processing performance of different diols after fermentation is presented in Fig. 3.

As can be observed, smaller initial product concentration in the fermentation broth results in higher costs, energy requirements and CO_2 emissions in the downstream process. This is in line with common observations such as those previously derived for the purification of volatile bioalcohols after fermentation.[28] However, it is noteworthy that the performance of the 1,4-BDO recovery process shows a slight deviation from the trends observed in the recovery processes of 1,3-PDO, 2,3-BDO, and 1,3-BDO. Specifically, the costs, energy consumption, and CO_2 emissions for 1,4-BDO recovery are lower than those for 1,3-BDO recovery, despite slightly lower product concentration in the broth. This is primarily attributed to the reduced presence of light and heavy impurities in the broth, which simplifies the separation process and lowers utility costs. Additionally, reduced wastewater treatment costs further contribute to the overall decrease in purification expenses. In conclusion, both concentration of the main product and level of impurities in the broth play crucial roles in determining the efficiency of downstream processing. Among these factors, the initial concentration of the main product has the greatest impact on the recovery process. However, a significant impurity load can significantly increase recovery costs by making the separation process more complex and raising waste treatment expenses. Nevertheless, if the fermentation broth contains considerable amounts of by-products, valorising these by-products could enhance the overall cost-effectiveness of the process. For instance, valorising by-products in the recovery of 1,3-PDO after fermentation reduced the total recovery costs (per kilogram of all recovered products) by 9–25%.[17]

Given that all considered diols have similar properties (e.g. composition in the fermentation broth, boiling points, etc.), it may be expected that one process design can be effectively used to purify all of them. This offers an interesting possibility of having one process capable of producing different diols depending on the current market demand.

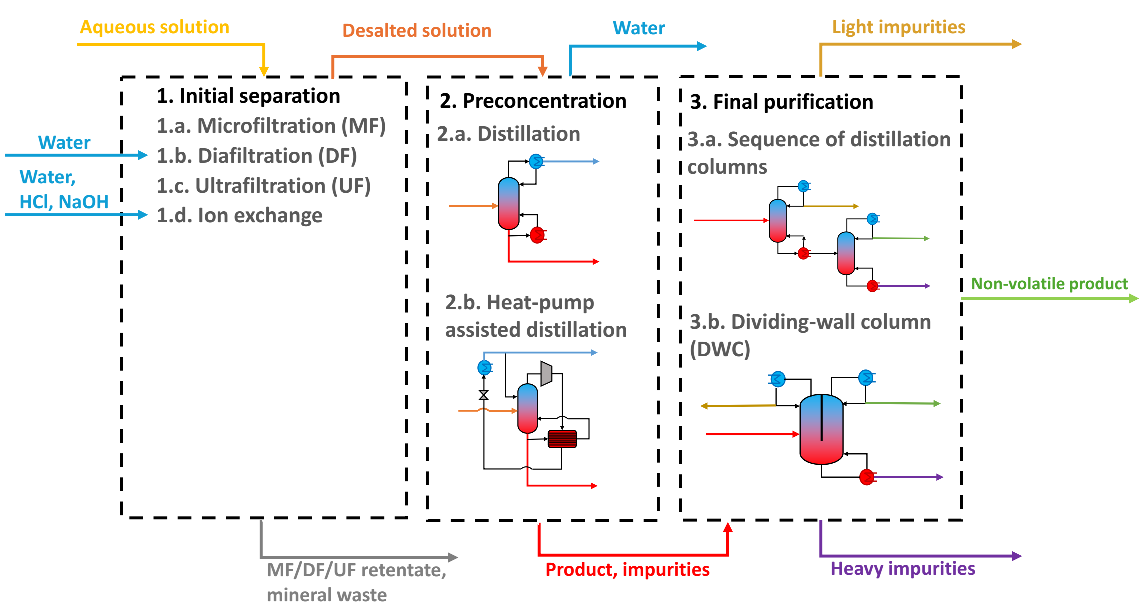

Figure 2. Generic block flow diagram for the purification of non-volatile products from the dilute aqueous stream.

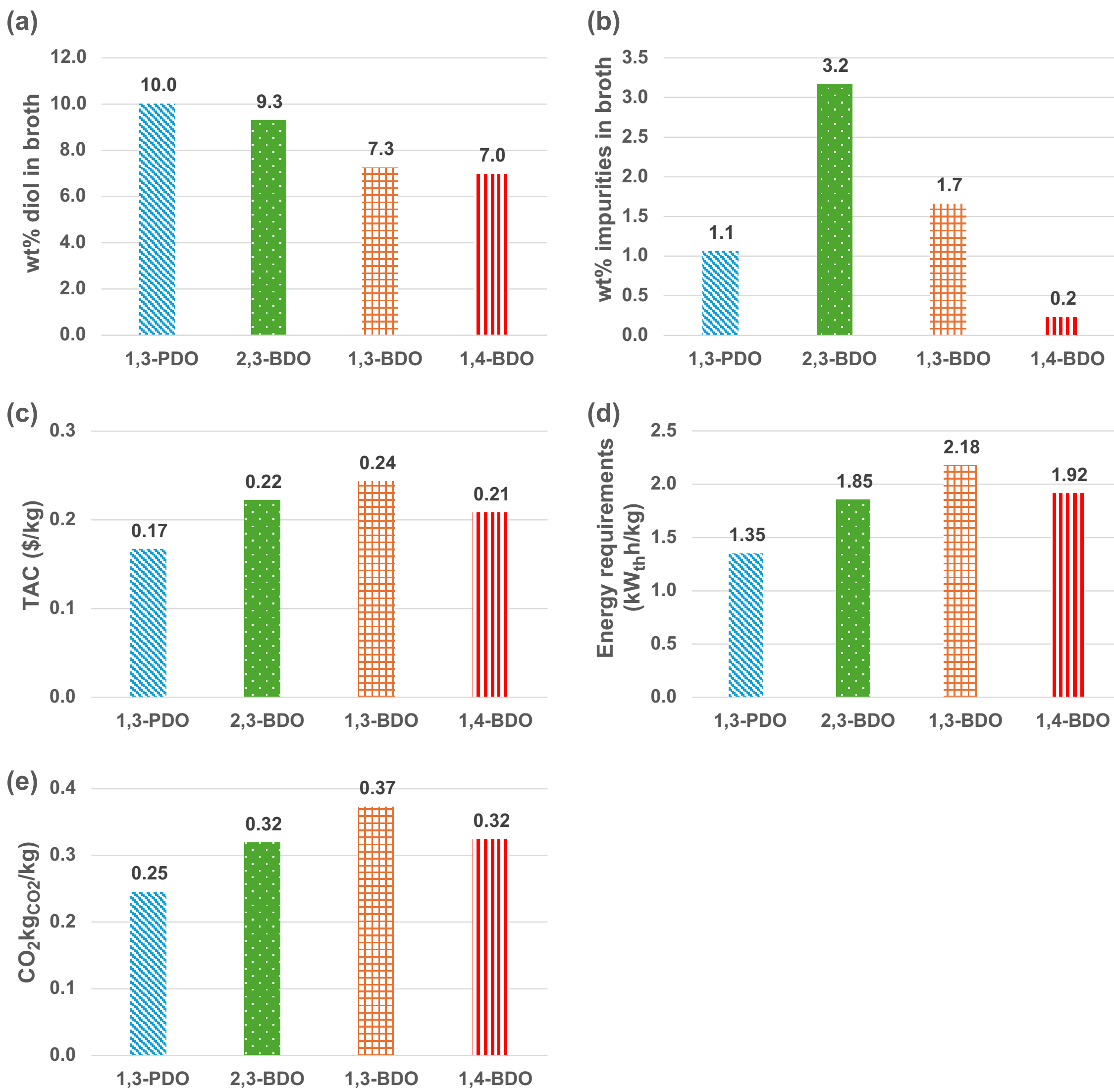

Figure 3. Assumed initial compositions and determined performance of the downstream processing for recovery of different diols after fermentation and initial separation: (a) wt.% of diol in the fermentation broth, (b) wt.% of impurities in the fermentation broth, (c) total annual purification costs (d) primary energy requirements and (e) CO_2 emissions (1,3-PDO, 1,3-propanediol; 2,3-BDO, 2,3-butanediol, 1,4-BDO, butanediol; 1,3-BDO, butanediol).

CONCLUSION

This perspective offers an important overview of the downstream processing performance in the recovery of non-volatile products after fermentation. It proposes a novel methodology for recovering high-boiling products from dilute aqueous streams in case light and heavy impurities are present. To minimize energy requirements, two steps are necessary in the downstream processing. Initially, most of the water with light impurities can be separated in the preconcentration step in a heat pump-assisted distillation column. Afterward, a valuable fermentation product can be recovered from the remaining water, light, and heavy impurities in the final purification in an integrated dividing-wall column. A proper choice of operating parameters in the preconcentration step should allow the implementation of the heat pump system. This would drastically reduce overall energy requirements, allow (green) electrification of the preconcentration step, and reduce equipment size in the final purification.

The developed methodology is applicable to the preconcentration and final purification steps in the recovery of different diols after fermentation. The higher concentrations of the diols in the broth generally lead to more cost-effective and energy-efficient downstream processing. Nonetheless, impurities in the broth additionally influence the downstream processing performance. Higher amounts of impurities complicate the separation process and increase economic and environmental costs.

Finally, similar downstream processing configuration that can effectively recover 1,3-PDO, 2,3-, 1,4- and 1,3-BDO offers an interesting opportunity to utilize a single process capable of producing different diols based on the current market demand.

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